Improvements in measurement of pH and titratable acidity

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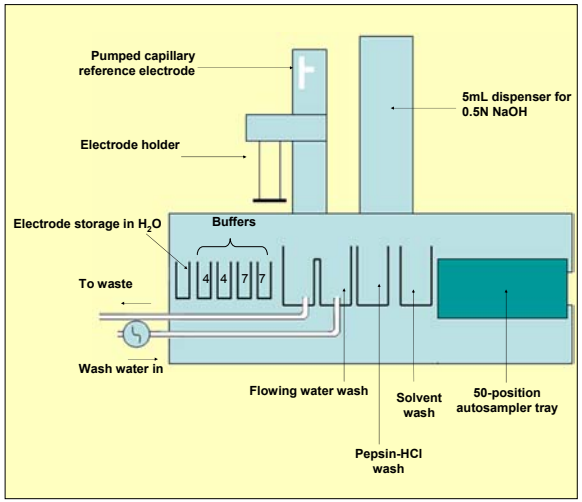
Summary

pH and Titratable Acidity (TA) are measured on grape juices, musts and wines at various stages of preparation. Sirius Vinotrate uses automation to improve the analysis of pH and TA. Samples of 10mL volume are pipetted into glass vials and placed in a 50-position autosampler. The instrument moves the pH electrode, overhead stirrer, quartz capillaries and temperature probe between buffer solutions, wash solutions and sample, such that no human handling is required. This automation brings significant improvements to the accuracy and reproducibility of measurement.

Samples are titrated with 0.5N NaOH solution; using this strong titrant reduces waste volumes. The use of tall, narrow vials enables pH of undiluted samples to be measured before titration. No pH meter is required.

During the development of this new instrument, we investigated automated techniques for de-gassing samples on the instrument, washing probes in flowing water between samples to eliminate carry-over, and cleaning probes to remove protein deposits. We also developed a novel reference electrode that does not get blocked in samples containing suspended particles.



CO_2 removal

Dissolved carbon dioxide would lead to an erroneously high TA readings, and is usually removed from samples by shaking under vacuum; while effective, this is an extra step before samples are titrated.

We investigated sparging 10 mL samples of wine with low pressure argon gas while situated on the instrument. A gas-tight seal with small leakage path above the vial ensures that atmospheric air is completely displaced while sparging. We found that a two-minute sparge was sufficient to remove titratable CO_2 from most samples with pH of 3 or below; longer sparges were required for some highly sparking wines.

Automatic washing

It is essential to wash probes between measurements to avoid carry-over.

Probes in Vinotrate are washed by moving them through a series of wash solutions. We found the optimum procedure for red and white wines was to wash for 5 seconds in flowing water, then for 5 seconds in pepsin-HCl solution (5% pepsin, 0.1N HCl), followed by another 5 seconds in flowing water. The first water wash removes the sample carry-over; the pepsin removes protein deposits from the pH electrode glass bulb; the second water wash removes pepsin-HCl. After following this wash procedure, no carry-over was observed.

Reference electrode improvements

Reference junction blockages when analysing samples containing suspended particles cause many pH electrode failures.

We have overcome these problems by introducing a pumped capillary reference electrode*. This double-junction electrode is attached to the tower, and connects to the sample through a quartz capillary. Before each pH measurement a small aliquot of filling solution is pumped through the capillary. No sign of electrode blockage was observed after analysing more than 500 wines and juices.

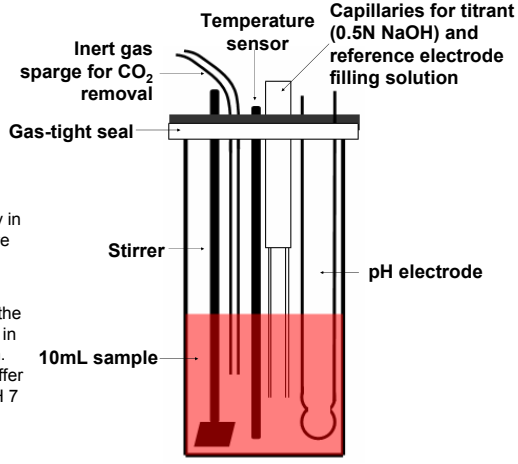
* patent applied for

Calibrating the pH electrode

The pH electrode is calibrated automatically in pH 4 and 7 buffer solutions. Calibrations are done at regular times, or after specified numbers of samples have been analyzed.

Probes are washed in flowing water and in the first vial of pH 4 buffer, and are then placed in the second vial of pH 4 buffer for calibration. They are then washed in water and pH7 buffer before being placed in the second vial of pH 7 buffer for calibration. This high-quality calibration procedure has been validated**.

** Comer, J E A. Hibbert, C. pH electrode performance under automated management conditions. Journal of Automatic Chemistry, 1997, 19, 213-224



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